Water Solubility and Solution Enthalpy of Polycyclic Aromatic Hydrocarbons

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Enthalpies of solution, ΔH_{sol}, for several polycyclic aromatic hydrocarbons (PAH) have been determined from experimental water solubility data. Water solubility values, as a function of temperature, were determined by a generator column method. In this method water was pumped through a column packed with a chromatographic support coated .with the PAH under study, producing a saturated aqueous solution of this. The solute in the saturated solution was extracted with a solid phase extractor column and analyzed, *on line*, by high performance liquid chromatography (Diode array detection coupled to fluorescence detection). Polycyclic aromatic hydrocarbons, as well as temperature ranges studied included anthracene (282.09 - 323.07 K), pyrene (281.69 - 305.43 K), 9,10-dihydroanthracene (278.12 - 313.17 K), 9,10-dihydrophenanthrene (277.96 - 298.16 K), m-terphenyl (278.00 - 323.13 K), and guaiazulene (277.62 - 303.13 K). The precision of water solubility measurements ranged between $\pm$ (0.2 to 4.6) %.

INTRODUCTION

The study of the solubility of highly hydrophobic compounds in water has become increasingly important in recent years. Hydrophobic interactions are generally considered to play a crucial role in the physical chemistry, biochemistry and environmental chemistry of non-polar organic compounds in aqueous systems. As a result, several processes including the dissolution of non-polar organic compounds in water, the environmental fate and toxicity of persistent organic chemicals in aquatic ecosystems have been tried to be described and explained in terms of the unfavorable interactions of these substances with water molecules. Therefore, it is necessary to try to understand the molecular forces and interactions involved when an organic compound dissolves in water.

In this work, a simple technique for determining accurate and precise water solubility data, S_w, of highly hydrophobic compounds is described. The method is based on pumping water through a thermostated generator column in order to generate emulsion-free, saturated aqueous solutions of the compound under study. Through a switching valve system the solute in the aqueous solution is extracted and concentrated by an *on-line* solid phase extraction process and subsequently eluted and analyzed by high performance liquid chromatography (fluorescence detection coupled to photodiode array detection).

Solubilities in water of six polycyclic aromatic compounds, PAHs, as a function of temperature are reported and compared, when possible, with literature data. A good agreement was found in the comparison between the S_w data determined in this work for anthracene and pyrene and the best available literature data. Apparently, no solubility data, as a function of temperature, have been determined previously for the other studied PAHs.

From the determined water solubility data as a function of temperature, the enthalpy of solution of each compound studied was determined.

EXPERIMENTAL SECTION.

Reagents

All the polycyclic aromatic hydrocarbons (PAHs) used in this work were obtained from Chem Service (West Chester, PA) with the following purities : anthracene (99.0 %), pyrene (98 %), 9,10-dihydrophenantrene (96.8 %), 9,10-dihydroanthracene (98 %), m-terphenyl (98.0 %), and guaiazulene (99 %). All they were used without further purification.

The water used in all the experiments was type-1 reagent water from a Nanopure deionizer (Barnstead Thermolyne). HPLC-grade acetonitrile from EM Science (Gibbs Town, NJ) was used during the liquid chromatographic analysis.

Columns for the generation (generator columns) of saturated aqueous solutions of the studied PAHs were constructed from stainless steel tubing (25 cm x 0.42 cm i.d.) fitted with stainless steel 2.0-μm fritted disks and zero dead volume reducing unions at each end. Columns were packed with Chromosorb W-HP, 100/120 mesh (Chromatography Research Supplies) coated with 0.4 wt % of the compound of interest. Previously to be used, Chromosorb W-HP was washed by Soxhlet extraction with acetonitrile and methanol. Coating of the solid support was accomplished by dissolving a known amount of PAH in methylene chloride, mixing with a known amount of Chromosorb, and stripping off the solvent in a rotary evaporator.

The solid phase extraction of PAHs in the generated aqueous solutions was done by using a stainless steel extraction columns (2 cm x 0.2 cm i.d.) home-packed with a 5-μm bonded C18 stationary phase (Spherisorb ODS-2 ; Waters Associates, Milford, Mass.). The packing procedure has already been described (Vera-Avila and Covarrubias, 1994). This kind of columns has shown a high extraction efficiency of PAHs from aqueous solutions (Vera-Avila and Covarrubias, 1994).

The studied PAHs were analyzed on a 25.0 cm x 0.46 cm i.d. analytical column packed with a bonded C18 stationary phase (Spherisorb S5 ODS-2; Waters Associates, Milford, Mass.). The chromatographic analysis was done with a Waters HPLC system consisting of a

Model 626 solvent delivery system with a model 600S controller, a model 474 fluorescence detector, a model 996 photodiode array detector, and a model 6324 Degassit (MetaChem Technologies) solvent degasser.

Experimental set up

The experimental set up used in this work for the determination of S_w data, as a function of temperature, is shown schematically in Figure 1.

Saturated solutions of the studied compounds were generated by pumping water through the generator column at flow rates ranging between 0.1 and 1.5 cm^3/min. The column was thermostated by means of a water bath (Julabo F70) controlled to ± 0.03 K. The use of the generator column allows to circumvent experimental difficulties related with the formation of clusters or aggregates of hydrophobic molecules in the water solutions.

The switching valve system in the experimental set up (figure 2) is composed of a 9725i Rheodyne injector and two 7000 Rheodyne switching valves. The injector, which is adapted with a constant volume loop, is used for injecting solutions of known concentration of each PAH (dissolved in acetonitrile) during the calibration steps.

The switching valve, **A**, is connected to the extraction column. This valve is the most important in the valve arrangement because allows both the extraction and the elution, *on-line*, of the solute in the saturated aqueous solution. A second switching valve, **B**, was incorporated into the system in order to prevent the unnecessary de-equilibration of both analytical and extraction columns during experimental determinations. Valve **B** allowed also to reduce the analysis time, as well as the solvent (mobile phase) consumption during each determination. All the lines in the set up shown were made of small-bore stainless steel tubing; 1/16" o.d. x 0.007" i. d. (1.59 mm o.d. x 0.178mm i.d.).

Extraction of the solute from the generated aqueous solution was accomplished by flowing a measured volume of that solution through the extraction column. After extraction,

the flow from the generator column was diverted to waste. Then, a suitable acetonitrile-water mixture from a HPLC system was pumped through the extraction column and the adsorbed compound was eluted towards the analytical column and the detectors.

The quantification of the PAHs in the saturated aqueous solutions was carried out by an external 7 to 8 point calibration. In order to reduce the error in the determined concentrations (Miller and Miller, 1988, Reza et al., 1999) the confidence limits of the calibration curve for each studied PAH was improved by constructing it in the narrowest possible concentration interval (usually setting the limits of the interval between approximately ± 60 % around the expected 25 ºC water solubility concentration, for a given standard sample size), and setting the expected water solubility concentrations, at the other temperatures, as close as possible to the center of the concentration interval. This was done by varying the size of the samples during the experimental S_w determinations in such a way that the size of the chromatographic peak obtained at the different studied temperatures was always approximately the same.

Each solubility data determined in this work represents the average of three to four individual solubility determinations

The errors associated with the other operational steps of the experimental procedure were also determined (Taylor, 1982) and found to range between 0.5 to 1.1 %. Quadratic addition of both chromatographic and operational errors yielded an uncertainty of 0.2 to 4.6 % for the S_w data determined in this work.

The within-run (three to four equilibrium samples collected during a single experiment, at each temperature) and between-run (experiments performed on different days, at several and even after periods of more that 1 month), precision of the method, as estimated by: $\pm$ $t_{a/2(n-1)}$ ($s/\sqrt{n}$) [where $t_{a/2(n-1)}$ is the **t** of Student with (n-1) degrees of freedom and a confidence level (α) of 95% ; **n** is the number of experimental solubility determinations (3 to 4), and **s** is the standard deviation of such determinations], was always better than $\pm 4.6\%$.

RESULTS AND DISCUSSION

Experimental water solubility data for the polycyclic aromatic hydrocarbons studied in this work are presented in table 1.

Table 1. Experimental water solubility data (expressed as mole fraction, **x**), of polycyclic aromatic hydrocarbons as a function of temperature

Anthracene		Pyrene	
T / K	$x / 10^{-8}$	T / K	$x / 10^{-8}$
282.09	0.15667	281.69	0.4221
284.72	0.18497	286.65	0.565°23
286.54	0.20013	287.61	0.61778
289.03	0.24865	283.54	0.50422
291.74	0.29009	289.85	0.71638
295.69	0.38005	291.2	0.7757
297.76	0.43868	294.68	0.96782
300.25	0.51044	302.81	1.5017
301.35	0.54582	298.7	1.1851
302.27	0.57109	300.51	1.3406
303.68	0.63982	305.43	1.7200
308.02	0.89959		
313.06	1.1695		
318.05	1.5859		
323.07	2.1459		

Guaiazulene		m-Terphenyl	
T / K	$x / 10^{-8}$	T / K	$x / 10^{-9}$
277.62	4.4435	278.00	0.70164
279.28	4.4928	280.79	0.90032

T / K	x	T / K	x
281.82	4.5756	284.95	0.93552
283.84	4.7138	288.13	1.4283
288.14	5.0526	293.10	1.7099
293.14	5.4501	298.14	2.3873
298.12	6.0211	303.15	3.1992
298.15	6.0318	308.15	4.1848
303.13	6.3063	313.22	5.7946
		318.22	7.4302
		323.13	9.0697

9,10-Dihydroanthracene

9,10-Dihydrophenantrene

T / K	$x\,/10^{-7}$	T / K	$x\,/\,10^{-7}$
278.12	0.4635	277.96	2.4906
279.01	0.47211	279.15	2.5826
281.41	0.52452	283.82	2.9064
284.11	0.59674	288.05	3.3302
285.21	0.63927	293.14	3.9948
288.11	0.76668	298.16	4.1727
291.16	0.89217		
294.12	1.0456		
297.75	1.3296		
299.41	1.4413		
302.21	1.6909		
305.82	2.0061		
309.44	2.3181		
313.17	2.6965		

Experimental water solubility data for anthracene and pyrene, as a function of temperature, have been widely reported (Wauchope and Getzen, 1972 ; Schwarz, 1977 ; May et al., 1978a,b ; May et al., 1983), even at high pressures and temperatures (Röβling and Franck,1983; Miller et al., 1998). However, despite the relatively large number of

studies many of the S_w data previously reported are only in partial agreement amongst themselves.

Experimental S_w values determined in this work for anthracene and pyrene show a very good agreement with those determined by a generator column technique (May et al., 1978a,b ; 1983). A direct comparison of 21 experimental S_w values for both anthracene and pyrene determined in this work, with S_w data obtained from the fitting of experimental values from May et al., (1978a,b ;1983) (determined between 5 to 30 ℃), showed to agree within ± 1.12 %.

Water solubility data for pyrene from this work are also in good agreement with those reported by Schwarz (1977) determined by a shake-flask technique. A comparison of 8 experimental solubility values determined in this work with S_w data obtained from the fitting of experimental values from Schwarz, 1977 (determined between 12.2 and 31.3 ℃) showed agreement within ± 3.4 %. However, S_w data determined in this work for anthracene are lower than those obtained from a batch stirring-contact method (Wauchope and Getzen, 1972, Schwarz, 1977). The latter is probably explained by considering that solubilities of highly hydrophobic substances determined by the shake flask method could be overestimated due to incomplete equilibration of the generated aqueous sample (Billington et al., 1983 ; deMaagd et al., 1998). Analysis of aqueous solutions by spectroscopic techniques could also affect accuracy of measurements because of the presence of dissolved impurities (May et al., 1978a).

By employing a vapor saturation method for preparing aqueous solutions, followed by liquid-liquid extraction and spectrophotometric analysis, Akiyoshi et al. (1987) determined the water solubility of m-terphenyl, at 25 ℃, to be $(1.186 \pm 0.004) \times 10^{-7}$ mole fraction. This value is higher than the one obtained in this work (table 1). However, these authors have pointed out, for other studied PAHs, that the generator column method gives extremely lower solubility values than those determined by its method. Even though their data were in agreement with results obtained by the shake flask method.

Apparently, no other experimental S_w data have been previously reported for the other PAHs studied in this work.

Dependencies of the solubility of the studied PAHs on temperature are presented in figure 3.

From figure 3 and table 1 it is possible to observe a very interesting behavior in the solubility of the studied PAHs. For example, the solubility of pyrene is grater than that of anthracene, even though the molecule of pyrene is larger and could be supposed to have a greater "hydrophobicity" than that of anthracene. On the other hand it can be observed that the solubility of phenenthrene (May et al., 1983) is larger than that of anthracene, even though both solids are chemically similar to each other.

When S_w data of phenanthrene (May et al., 1978a,b) are compared with the corresponding values of its partially-saturated isomer 9,10-dihydrophenanthrene it is found that, in the temperature range from 278 to 298 K, 9,10-dihydrophenanthrene is notably more soluble than phenanthrene. The increase in the S_w values by partial saturation of the molecule it is also observed in the case of anthracene and 9,10-dihidroanthracene. Partial saturation of anthracene in the carbons 9 and 10 provokes an increase in its water solubility of about one order of magnitude in mole fraction.

In order to understand the above mentioned behaviours, it could be valuable to explore the contributions of solute-solute and solute-water interactions in the aqueous solution process, through the analysis of the standard thermodynamic properties for the solution process, such as enthalpies, entropies and free energies of a liquid chemical or subcooled liquid chemical (for solids) (Zhang and Gobas., 1995).

Estimation of enthalpies of solution from water solubility data can be done by using the following equation (Zhang and Gobas, 1995) :

$$\Delta H_{s,i} = -R\left(\frac{\partial \ln x_i}{\partial (1/T)}\right)_P - \Delta H_{f,i}$$

(1)

with

$$\Delta H_{f,i} = \Delta H_{f,i}(T_m) + \int_{T}^{Tm} \Delta C_P \ dT$$

where x_i is the mole fraction solubility of solute i in water, ΔC_P is the difference between the heat capacity of the hypothetical subcooled liquid C_{pl} and the heath capacity of solid solute C_{ps}, and $\Delta H_{f,i}$ is the enthalpy of fusion of i. The difference ΔC_P is often assumed to be relatively insensitive to temperature (Granberg and Rasmuson, 1999).

Values of enthalpy of solution for anthracene and pyrene were estimated from the solubility data. The values for the enthalpies were corrected to those for subcooled solids by substacting the heat of fusion (Wuachope and Getzen 1972) of each compound from the values determined from the ln S_w (x) vs 1/T curves (figure 2). ΔH_{sol}, values are give in table 2. Other values of ΔH_{sol} previously reported are also included for comparative purposes.

Table 2. Enthalpies of solution , ΔH_{sol}, of anthracene and pyrene

Reference	Enthalpy of Solution / kJ mol^{-1}	
	Anthracene	Pyrene
Schwarzenbach et al., 1993[ξ]	18.4	26.4
Zhang and Gobas, 1995[φ]	15.06, 20.04 19.6	17.4, 31.13
This work[ξ,ψ]	19.9 ± 1.4	26.8 ± 1.5

[ξ] Enthalpies of fusion were taken from Wuachope and Getzen (1972)

[φ] Quoted by Zhang and Gobas (1995) from several references

[ψ] Estimated from solubility measurements between 282 to 323 K for anthracene and 281 to 305 K for pyrene

As shown in table 2 the ΔH_{sol} value for anthracene estimated in this work is in good agreement with most of the previously reported values. The value for pyrene is also in agreement with that reported by Schwarzenbach et al.(1993). Evidently, data of ΔH_{sol} for

pyrene quoted by Zhang and Gobas (1995) does not show a good agreement amongst themselves.

For anthracene and pyrene, as well as for the other studied PAHs, the enthalpy change does not vary widely with temperature, as illustrated by the straight line behavior in figure 3.

The enthalpy of solution estimated for the other PAHs, in the temperature range studied, is given in table 3.

Table 3. Enthalpies of solution of polycyclic aromatic hydrocarbons

PAH	Enthalpy of Solution / kJ mol^{-1}
9,10-Dihydroanthracene	38.1 ± 1.2
9,10-Dihydrophenanthrene	18.7 ± 3.4
Guaiazulene	10.4 ± 1.1
m-Terphenyl	43.0 ± 2.3

These values were not corrected to those for subcooled liquids because experimental values of heats of fusion were not available. The final aim of determining such values is in order to generate new data of thermodynamic parameters which can be useful to understand the forces and interactions involved when a very hydrophobic compound dissolves in water.

CONCLUSIONS

A method for the determination of precise and accurate water solubility data of sparingly soluble hydrophobic compounds, as a function of temperature has been described.

The method ensures the generation of stable saturated aqueous solutions of the studied compounds, at a given temperature, and allows its accurate and precise analysis through an *on-line* solid phase extraction-elution system. The reported set up minimizes adsorptive and evaporative losses of the solute, as well as the introduction of impurities in the experimental arrangement. It also reduces the contact of the operator with harmful compounds and optimizes the use of organic mobile phases.

The precision of several S_w determinations performed during a single experiment (single day), at each temperature, as well as the precision of determinations performed on different days, are better than $\pm 4.6\%$.

Solubility data for anthracene and pyrene determined in this work are in good agreement with the best S_w literature values previously reported. The method has also been used to determine new data of water solubility for m-terphenyl, 9,10-dihydrophenanthrene, 9,10-dihydroanthracene and guaiazulene. No experimental S_w values, as a function of temperature, have been previously reported for these PAHs.

From the experimental S_w values, the enthalpy of solution of each studied PAH in water has been determined. The values for the enthalpies have not been corrected yet to those for subcooled solids, because of the lack of heats of fusion for the solid hydrocarbons. However, these values will be useful both in environmental studies and in the thermodynamic understanding of the dissolution process of hydrophobic organics in water.

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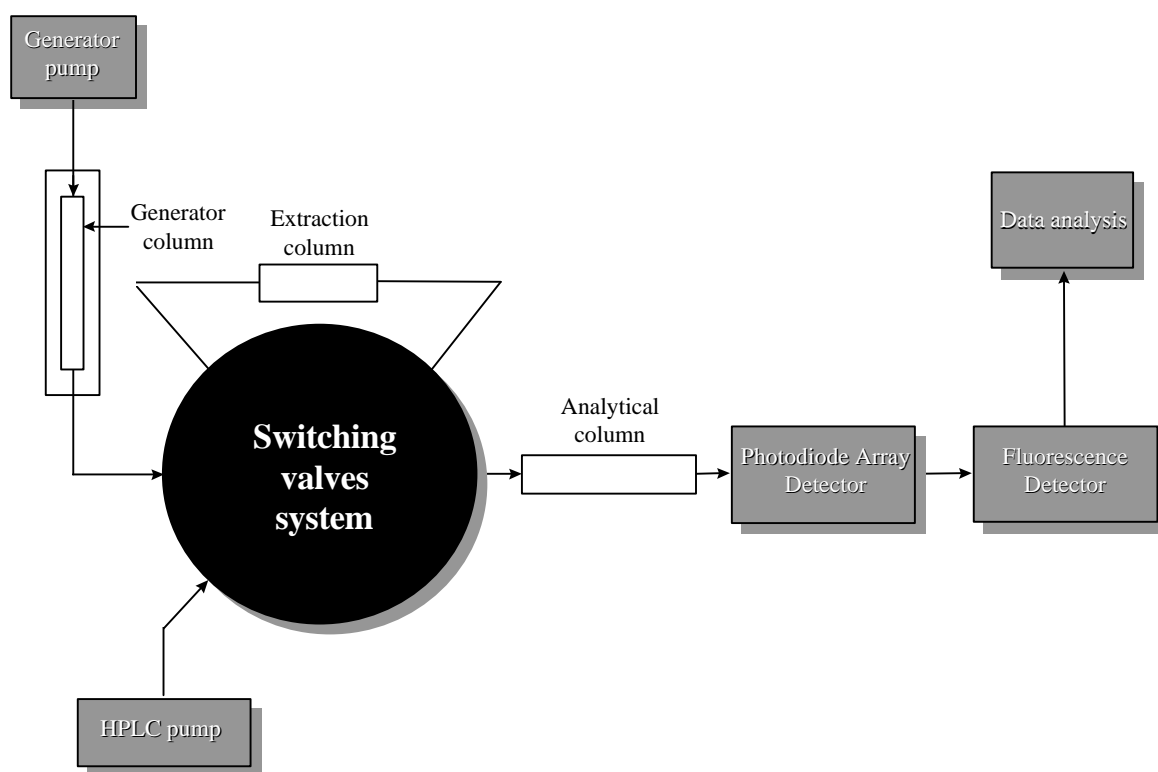
Figure 1. Experimental set up for the determination of water solubility data as a function of temperature
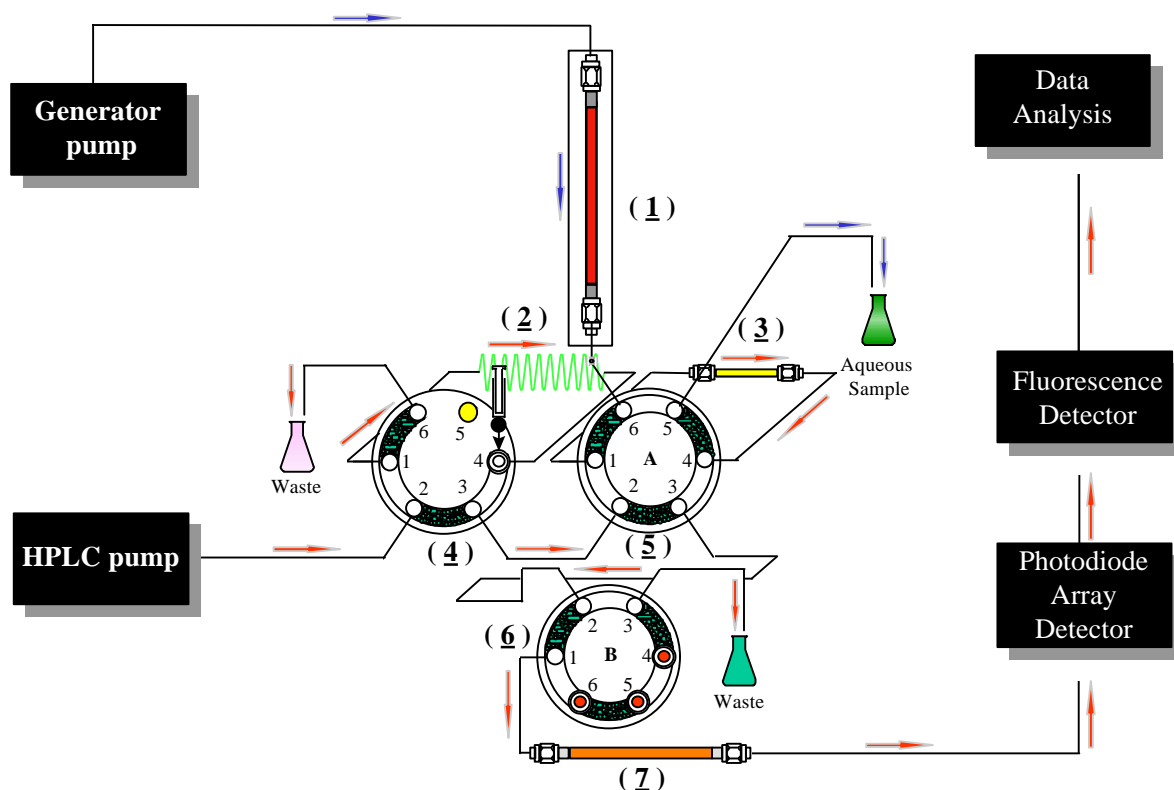
Figure 2. Switching valve system. (1) Generator column, (2) Constant volume loop, (3) Extraction column, (4) Injector, (5,6) Switching valves, (7) Analytical column.
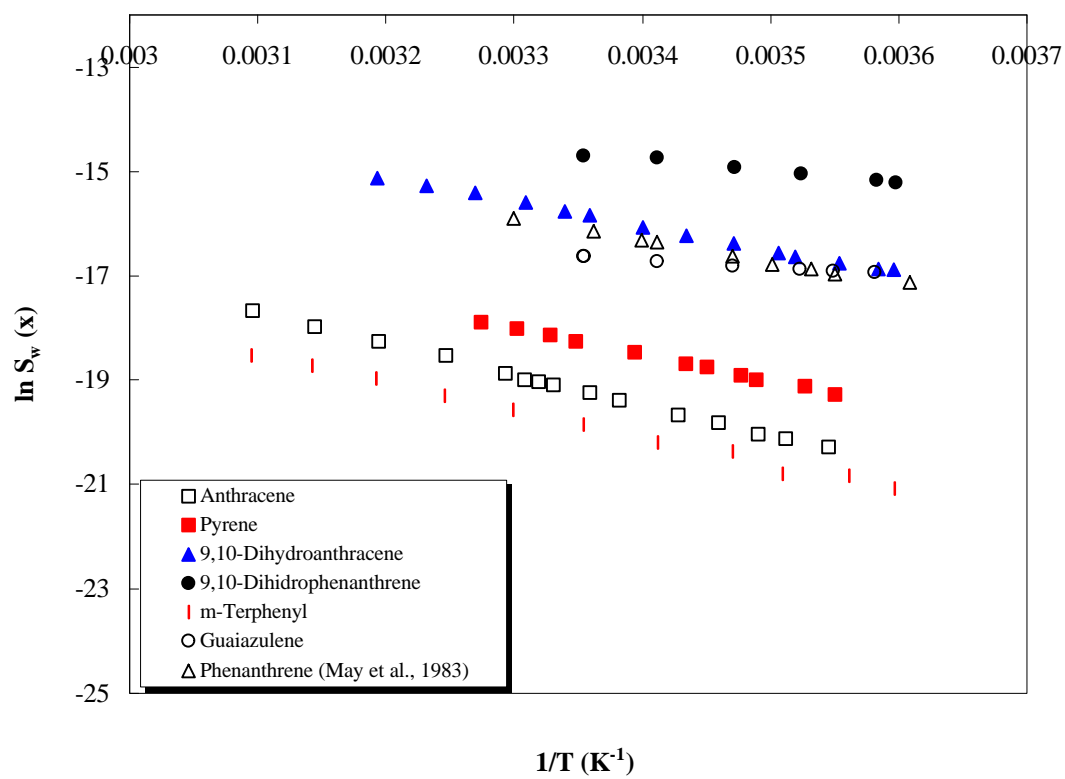
Figure 3. Dependencies on the solubility of some PAHs on temperature